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(21) International Application Number: PCT/US93/02038 (22) International Filing Date: 9 March 1993 (09.03.93)  (30) Priority data: 854,172                      20 March 1992 (20.03.92)                      US  (71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).  (72) Inventor: CHERPECK, Richard, E. ; 8962 Cypress Avenue, Cotati, CA 94931 (US).  (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).		(81) Designated States: AU, BR, CA, FI, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published <i>With international search report.</i>
(54) Title: FUEL ADDITIVE COMPOSITIONS CONTAINING POLY(OXYALKYLENE) AMINES AND POLYALKYL HYDROXYAROMATICS  (57) Abstract  A fuel additive composition comprising: a) a poly(oxyalkylene) amine having at least one basic nitrogen and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel range; and b) a polyalkyl hydroxyaromatic compound or salt thereof wherein the polyalkyl group has sufficient molecular weight and carbon chain length to render the polyalkyl hydroxyaromatic compound soluble in hydrocarbons boiling in the gasoline or diesel range.		

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FUEL ADDITIVE COMPOSITIONS CONTAINING  
POLY(OXYALKYLENE) AMINES  
AND POLYALKYL HYDROXYAROMATICS

BACKGROUND OF THE INVENTION

This invention relates to a fuel additive composition. More particularly, this invention relates to a fuel additive composition containing a poly(oxyalkylene) amine and a polyalkyl hydroxyaromatic compound.

It is well known in the art that liquid hydrocarbon combustion fuels, such as fuel oils and gasolines, tend to exhibit certain deleterious characteristics, either after long periods of storage or under actual operational conditions. Gasolines, for example, in operational use tend to deposit sludge and varnish at various points in the power system, including the carburetor or injectors and the intake valves. It is desirable, therefore, to find a means for improving liquid hydrocarbon fuels by lessening their tendency to leave such deposits.

U.S. Patent No. 3,849,085 discloses a motor fuel composition comprising a mixture of hydrocarbon in the gasoline boiling range containing about 0.01 to 0.25 volume percent of a high molecular weight aliphatic hydrocarbon substituted phenol in which the aliphatic hydrocarbon radical has an average molecular weight in the range of about 500 to 3,500. This patent teaches that gasoline compositions containing a minor amount of an aliphatic hydrocarbon substituted phenol not only prevents or inhibits the formation of intake valve and port deposits in a gasoline engine but also enhances the performance of the fuel composition in engines designed to operate at higher operating temperatures with a minimum of

01 decomposition and deposit formation in the manifold of the  
02 engine.

03

04 U.S. Patent No. 4,134,846 discloses a fuel additive  
05 composition comprising a mixture of (1) the reaction product  
06 of an aliphatic hydrocarbon-substituted phenol,  
07 epichlorohydrin and a primary or secondary mono- or  
08 polyamine, and (2) a polyalkylene phenol. This patent  
09 teaches that such compositions show excellent carburetor,  
10 induction system and combustion chamber detergency and, in  
11 addition, provide effective rust inhibition when used in  
12 hydrocarbon fuels at low concentrations.

13

14

SUMMARY OF THE INVENTION

15

16 The present invention provides a novel fuel additive  
17 composition comprising:

18

19 (a) a poly(oxyalkylene) amine having at least one basic  
20 nitrogen atom and a sufficient number of oxyalkylene  
21 units to render the poly(oxyalkylene) amine soluble in  
22 hydrocarbons boiling in the gasoline or diesel range,  
23 and

24

25 (b) a polyalkyl hydroxyaromatic compound or salt thereof  
26 wherein the polyalkyl group has sufficient molecular  
27 weight and carbon chain length to render the polyalkyl  
28 hydroxyaromatic compound soluble in hydrocarbons  
29 boiling in the gasoline or diesel range.

30

31 The present invention further provides a fuel composition  
32 comprising a major amount of hydrocarbons boiling in the  
33 gasoline or diesel range and an effective detergent amount  
34 of the novel fuel additive composition described above.

01 The present invention is also concerned with a fuel  
02 concentrate comprising an inert stable oleophilic organic  
03 solvent boiling in the range of from about 150°F to 400°F  
04 and from about 10 to 70 weight percent of the fuel additive  
05 composition of the instant invention.

06  
07 Among other factors, the present invention is based on the  
08 surprising discovery that the unique combination of a  
09 poly(oxyalkylene) amine and a polyalkyl hydroxyaromatic  
10 compound provides unexpectedly superior deposit control  
11 performance when compared to each component individually.

12

13 DETAILED DESCRIPTION OF THE INVENTION

14

15 The Poly(oxyalkylene) Amine

16

17 As noted above, the poly(oxyalkylene) amine component of the  
18 present fuel additive composition is a poly(oxyalkylene)  
19 amine having at least one basic nitrogen atom and a  
20 sufficient number of oxyalkylene units to render the  
21 poly(oxyalkylene) amine soluble in hydrocarbons boiling in  
22 the gasoline or diesel range. Preferably, such  
23 poly(oxyalkylene) amines will also be of sufficient  
24 molecular weight so as to be nonvolatile at normal engine  
25 intake valve operating temperatures, which are generally in  
26 the range of about 175°C to 300°C.

27

28 Generally, the poly(oxyalkylene) amines suitable for use in  
29 the present invention will contain at least about 5  
30 oxyalkylene units, preferably about 5 to 100, more  
31 preferably about 8 to 100, and even more preferably about 10  
32 to 100. Especially preferred poly(oxyalkylene) amines will  
33 contain about 10 to 25 oxyalkylene units.

34

01 The molecular weight of the presently employed  
02 poly(oxyalkylene) amines will generally range from about 500  
03 to about 10,000, preferably from about 500 to about 5,000.

04  
05 Suitable poly(oxyalkylene) amine compounds include  
06 hydrocarbyl poly(oxyalkylene) polyamines as disclosed, for  
07 example, in U.S. Patent No. 4,247,301 to Honnen, the  
08 disclosure of which is incorporated herein by reference.  
09 These compounds are hydrocarbyl poly(oxyalkylene) polyamines  
10 wherein the poly(oxyalkylene) moiety comprises at least one  
11 hydrocarbyl-terminated poly(oxyalkylene) chain of 2 to 5  
12 carbon atom oxyalkylene units, and wherein the  
13 poly(oxyalkylene) chain is bonded through a terminal carbon  
14 atom to a nitrogen atom of a polyamine having from 2 to  
15 about 12 amine nitrogen atoms and from 2 to about 40 carbon  
16 atoms with a carbon-to-nitrogen ratio between about 1:1 and  
17 10:1. The hydrocarbyl group on these hydrocarbyl  
18 poly(oxyalkylene) polyamines will contain from about 1 to 30  
19 carbon atoms. These compounds generally have molecular  
20 weights in the range of about 500 to 10,000, preferably from  
21 about 500 to 5,000 and more preferably from about 800 to  
22 5,000.

23

24 The above-described hydrocarbyl poly(oxyalkylene) polyamines  
25 are prepared by conventional procedures known in the art, as  
26 taught, for example, in U.S. Patent No. 4,247,301.

27

28 Other poly(oxyalkylene) amines suitable for use in the  
29 present invention are the poly(oxyalkylene) polyamines  
30 wherein the poly(oxyalkylene) moiety is connected to the  
31 polyamine moiety through an oxyalkylene hydroxy-type linkage  
32 derived from an epihalohydrin, such as epichlorohydrin or  
33 epibromohydrin. This type of poly(oxyalkylene) amine having  
34 an epihalohydrin-derived linkage is described, for example,

01 in U.S. Patent No. 4,261,704, the disclosure of which is  
 02 incorporated herein by reference.

03

04 Useful polyamines for preparing the epihalohydrin-derived  
 05 poly(oxyalkylene) polyamines include, for example, alkylene  
 06 polyamines, polyalkylene polyamines, cyclic amines, such as  
 07 piperazines, and amino-substituted amines. The  
 08 poly(oxyalkylene) polyamines having an epihalohydrin-derived  
 09 linkage between the poly(oxyalkylene) and polyamine moieties  
 10 are prepared using known procedures as taught, for example,  
 11 in U.S. Patent No. 4,261,704.

12

13 Another type of poly(oxyalkylene) amine useful in the  
 14 present invention is a highly branched alkyl  
 15 poly(oxyalkylene) monoamine as described, for example in  
 16 published European Patent Application No. 0,448,365 A1,  
 17 published September 25, 1991, the disclosure of which is  
 18 incorporated herein by reference. These highly branched  
 19 alkyl poly(oxyalkylene) monoamines have the general formula:

20



22

23 wherein R is a highly branched alkyl group containing from  
 24 12 to 40 carbon atoms, preferably an alkyl group having 20  
 25 carbon atoms which is derived from a Guerbet condensation  
 26 reaction, and x is a number up to 30, preferably 4 to 8.  
 27 The preferred alkyl group is derived from a Guerbet alcohol  
 28 containing 20 carbon atoms having the formula:

29



32

33 wherein R'' is a hydrocarbyl chain.

34

01 The above highly branched alkyl poly(oxyalkylene) monoamines  
02 are prepared by using known methods as disclosed, for  
03 example, in European Patent Application No. 0,448,365 A1.  
04

05 A preferred class of poly(oxyalkylene) amine suitable for  
06 use in the composition of the present invention is the  
07 hydrocarbyl-substituted poly(oxyalkylene) aminocarbamate  
08 disclosed, for example, in U.S. Patent Nos. 4,288,612;  
09 4,236,020; 4,160,648; 4,191,537; 4,270,930; 4,233,168;  
10 4,197,409; 4,243,798 and 4,881,945, the disclosure of each  
11 of which are incorporated herein by reference. These  
12 hydrocarbyl poly(oxyalkylene) aminocarbamates will contain  
13 at least one basic nitrogen atom and have an average  
14 molecular weight of about 500 to 10,000, preferably about  
15 500 to 5,000, and more preferably about 1,000 to 3,000. As  
16 discussed more fully below, these hydrocarbyl  
17 poly(oxyalkylene) aminocarbamates can be said to contain a  
18 poly(oxyalkylene) component, an amine component and a  
19 carbamate connecting group.  
20

21 A. The Poly(oxyalkylene) Component  
22

23 The hydrocarbyl-terminated poly(oxyalkylene) polymers which  
24 are utilized in preparing the amino carbamates employed in  
25 the present invention are monohydroxy compounds, e.g.,  
26 alcohols, often termed monohydroxy polyethers, or  
27 polyalkylene glycol monocarbyl ethers, or "capped"  
28 poly(oxyalkylene) glycols, and are to be distinguished from  
29 the poly(oxyalkylene) glycols (diols), or polyols, which are  
30 not hydrocarbyl-terminated, i.e., are not capped. The  
31 hydrocarbyl-terminated poly(oxyalkylene) alcohols are  
32 produced by the addition of lower alkylene oxides, such as  
33 oxirane, ethylene oxide, propylene oxide, butylene oxide,  
34 etc. to the hydroxy compound, ROH, under polymerization

01 conditions, wherein R is the hydrocarbyl group which caps  
02 the poly(oxyalkylene) chain. In the poly(oxyalkylene)  
03 component employed in the present invention, the group R  
04 will generally contain from 1 to about 30 carbon atoms,  
05 preferably from 2 to about 20 carbon atoms and is preferably  
06 aliphatic or aromatic, i.e., an alkyl or alkyl phenyl  
07 wherein the alkyl is a straight or branched-chain of from  
08 1 to about 24 carbon atoms. More preferably, R is  
09 alkylphenyl wherein the alkyl group is a branched-chain of  
10 12 carbon atoms, derived from propylene tetramer, and  
11 commonly referred to as tetrapropenyl. The oxyalkylene  
12 units in the poly(oxyalkylene) components preferably contain  
13 from 2 to about 5 carbon atoms but one or more units of a  
14 larger carbon number may also be present. Generally, each  
15 poly(oxyalkylene) polymer contains at least about 5  
16 oxyalkylene units, preferably about 5 to about 100  
17 oxyalkylene units, more preferably about 8 to about 100  
18 units, even more preferably about 10 to 100 units, and most  
19 preferably 10 to about 25 such units. The poly(oxyalkylene)  
20 component employed in the present invention is more fully  
21 described and exemplified in U.S. Patent No. 4,191,537, the  
22 disclosure of which is incorporated herein by reference.

23  
24 Although the hydrocarbyl group on the hydrocarbyl  
25 poly(oxyalkylene) component will preferably contain from  
26 1 to about 30 carbon atoms, longer hydrocarbyl groups,  
27 particularly longer chain alkyl phenyl groups, may also be  
28 employed.

29  
30 For example, alkylphenyl poly(oxyalkylene) aminocarbamates  
31 wherein the alkyl group contains at least 40 carbon atoms,  
32 as described in U.S. Patent No. 4,881,945 to Buckley, are  
33 also contemplated for use in the present invention. The  
34 alkyl phenyl group on the aminocarbamates of U.S. Patent

01 No. 4,881,945 will preferably contain an alkyl group of  
02 50 to 200 carbon atoms, and more preferably, an alkyl group  
03 of 60 to 100 carbon atoms. The disclosure of U.S. Patent  
04 No. 4,881,945 is incorporated herein by reference.  
05

06 Also, contemplated for use in the present invention are  
07 alkylphenyl poly(oxypropylene) aminocarbamates wherein the  
08 alkyl group is a substantially straight-chain alkyl group  
09 of about 25 to 50 carbon atoms derived from an alpha olefin  
10 oligomer of  $C_4$  to  $C_{20}$  alpha olefins, as described in  
11 PCT International Patent Application Publication No. WO  
12 90/07564, published July 12, 1990, the disclosure of which  
13 is incorporated herein by reference.  
14

15 B. The Amine Component  
16

17 The amine moiety of the hydrocarbyl-terminated  
18 poly(oxyalkylene) aminocarbamate is preferably derived from  
19 a polyamine having from 2 to about 12 amine nitrogen atoms  
20 and from 2 to about 40 carbon atoms. The polyamine is  
21 preferably reacted with a hydrocarbyl poly(oxyalkylene)  
22 chloroformate to produce the hydrocarbyl poly(oxyalkylene)  
23 aminocarbamate fuel additive finding use within the scope of  
24 the present invention. The chloroformate is itself derived  
25 from hydrocarbyl poly(oxyalkylene) alcohol by reaction with  
26 phosgene. The polyamine, encompassing diamines, provides  
27 the product poly(oxyalkylene) aminocarbamate with, on the  
28 average, at least about one basic nitrogen atom per  
29 carbamate molecule, i.e., a nitrogen atom titratable by  
30 strong acid. The polyamine preferably has a carbon-to-  
31 nitrogen ratio of from about 1:1 to about 10:1. The  
32 polyamine may be substituted with substituents selected from  
33 hydrogen, hydrocarbyl groups of from 1 to about 10 carbon  
34 atoms, acyl groups of from 2 to about 10 carbon atoms, and

01 monoketone, monohydroxy, mononitro, monocyano, alkyl and  
02 alkoxy derivatives of hydrocarbyl groups of from 1 to 10  
03 carbon atoms. It is preferred that at least one of the  
04 basic nitrogen atoms of the polyamine is a primary or  
05 secondary amino nitrogen. The polyamine component employed  
06 in the present invention has been described and exemplified  
07 more fully in U.S. Patent No. 4,191,537.

08

09 Hydrocarbyl, as used in describing the hydrocarbyl  
10 poly(oxyalkylene) and amine components used in this  
11 invention, denotes an organic radical composed of carbon and  
12 hydrogen which may be aliphatic, alicyclic, aromatic or  
13 combinations thereof, e.g., aralkyl. Preferably, the  
14 hydrocarbyl group will be relatively free of aliphatic  
15 unsaturation, i.e., ethylenic and acetylenic, particularly  
16 acetylenic unsaturation. The more preferred polyamine  
17 finding use within the scope of the present invention is a  
18 polyalkylene polyamine, including alkylenediamine, and  
19 including substituted polyamines, e.g., alkyl and  
20 hydroxyalkyl-substituted polyalkylene polyamine.  
21 Preferably, the alkylene group contains from 2 to 6 carbon  
22 atoms, there being preferably from 2 to 3 carbon atoms  
23 between the nitrogen atoms. Examples of such polyamines  
24 include ethylenediamine, diethylene triamine, triethylene  
25 tetramine, di(trimethylene) triamine, dipropylene triamine,  
26 tetraethylene pentamine, etc. Among the polyalkylene  
27 polyamines, polyethylene polyamine and polypropylene  
28 polyamine containing 2-12 amine nitrogen atoms and 2-24  
29 carbon atoms are especially preferred and in particular, the  
30 lower polyalkylene polyamines, e.g., ethylenediamine,  
31 diethylene triamine, propylene diamine, dipropylene  
32 triamine, etc., are most preferred.

33

34

01 C. The Aminocarbamate

02

03 The poly(oxyalkylene) aminocarbamate fuel additive used in  
04 compositions of the present invention is obtained by linking  
05 the amine component and the poly(oxyalkylene) component  
06 together through a carbamate linkage, i.e.,

07

08

09



10

11 wherein the oxygen may be regarded as the terminal hydroxyl  
12 oxygen of the poly(oxyalkylene) alcohol component, and the  
13 carbonyl group  $\text{---C(O)---}$ , is preferably provided by a  
14 coupling agent, e.g., phosgene. In the preferred method of  
15 preparation, the hydrocarbyl poly(oxyalkylene) alcohol is  
16 reacted with phosgene to produce a chloroformate and the  
17 chloroformate is reacted with the polyamine. The carbamate  
18 linkages are formed as the poly(oxyalkylene) chains are  
19 bound to the nitrogen of the polyamine through the  
20 oxycarbonyl group of the chloroformate. Since there may be  
21 more than one nitrogen atom of the polyamine which is  
22 capable of reacting with the chloroformate, the  
23 aminocarbamate contains at least one hydrocarbyl  
24 poly(oxyalkylene) polymer chain bonded through an  
25 oxycarbonyl group to a nitrogen atom of the polyamine, but  
26 the carbonate may contain from 1 to 2 or more such chains.  
27 It is preferred that the hydrocarbyl poly(oxyalkylene)  
28 aminocarbamate product contains on the average, about  
29 1 poly(oxyalkylene) chain per molecule (i.e., is a  
30 monocarbamate), although it is understood that this reaction  
31 route may lead to mixtures containing appreciable amounts of  
32 di or higher poly(oxyalkylene) chain substitution on a  
33 polyamine containing several reactive nitrogen atoms. A  
34 particularly preferred aminocarbamate is alkylphenyl

01 poly(oxybutylene) aminocarbamate, wherein the amine moiety  
02 is derived from ethylene diamine or diethylene triamine.  
03 Synthetic methods to avoid higher degrees of substitution,  
04 methods of preparation, and other characteristics of the  
05 aminocarbamates used in the present invention are more fully  
06 described and exemplified in U.S. Patent No. 4,191,537.  
07

08 The Polyalkyl Hydroxyaromatic Compound  
09

10 As noted above, the polyalkyl hydroxyaromatic component of  
11 the present fuel additive composition is a polyalkyl  
12 hydroxyaromatic compound or salt thereof wherein the  
13 polyalkyl group has sufficient molecular weight and carbon  
14 chain length to render the polyalkyl hydroxyaromatic  
15 compound soluble in hydrocarbons boiling in the gasoline or  
16 diesel range. As with the poly(oxyalkylene) amine component  
17 of the present invention, the polyalkyl hydroxyaromatic  
18 compound will preferably be of sufficient molecular weight  
19 so as to be nonvolatile at normal engine intake valve  
20 operating temperatures, generally in the range of about  
21 175°C to 300°C.  
22

23 In general, the polyalkyl substituent on the polyalkyl  
24 hydroxyaromatic compound will have an average molecular  
25 weight in the range of about 400 to 5,000, preferably about  
26 400 to 3,000, more preferably from about 600 to 2,000.  
27

28 The polyalkyl-substituted hydroxyaromatic compounds finding  
29 use in this invention are derived from hydroxyaromatic  
30 hydrocarbons. Such hydroxyaromatic compounds include  
31 mononuclear monohydroxy and polyhydroxy aromatic  
32 hydrocarbons having 1 to 4, and preferably 1 to 3, hydroxy  
33 groups. Suitable hydroxyaromatic compounds include phenol,  
34

01 catechol, resorcinol, hydroquinone, pyrogallol, and the  
02 like. The preferred hydroxyaromatic compound is phenol.  
03

04 Suitable polyalkyl hydroxyaromatic compounds and their  
05 preparation are described, for example, in U.S. Patent  
06 Nos. 3,849,085; 4,231,759 and 4,238,628, the disclosures of  
07 each of which are incorporated herein by reference.  
08

09 The polyalkyl substituent on the polyalkyl hydroxyaromatic  
10 compounds employed in the invention may be generally derived  
11 from polyolefins which are polymers or copolymers of  
12 mono-olefins, particularly 1-mono-olefins, such as ethylene,  
13 propylene, butylene, and the like. Preferably, the  
14 mono-olefin employed will have 2 to about 24 carbon atoms,  
15 and more preferably, about 3 to 12 carbon atoms. More  
16 preferred mono-olefins include propylene, butylene,  
17 particularly isobutylene, 1-octene and 1-decene.  
18 Polyolefins prepared from such mono-olefins include  
19 polypropylene, polybutene, especially polyisobutene, and the  
20 polyalphaolefins produced from 1-octene and 1-decene.  
21

22 The preferred polyisobutenes used to prepare the presently  
23 employed polyalkyl hydroxyaromatic compounds are  
24 polyisobutenes which comprise at least about 20% of the more  
25 reactive methylvinylidene isomer, preferably at least 50%  
26 and more preferably at least 70%. Suitable polyisobutenes  
27 include those prepared using BF<sub>3</sub> catalysts. The preparation  
28 of such polyisobutenes in which the methylvinylidene isomer  
29 comprises a high percentage of the total composition is  
30 described in U.S. Patent Nos. 4,152,499 and 4,605,808.  
31

32 Examples of suitable polyisobutenes having a high  
33 alkylvinylidene content include Ultravis 30, a polyisobutene  
34 having a molecular weight of about 1300 and a

01 methylvinylidene content of about 74%, available from  
02 British Petroleum.  
03

04 Numerous methods are known for preparing the polyalkyl  
05 hydroxyaromatic compounds used in the present invention and  
06 any of these are considered suitable for producing the  
07 polyalkyl hydroxyaromatic component of the instant fuel  
08 additive composition. One such method involves the reaction  
09 of a phenol with an olefin polymer in the presence of an  
10 aluminum chloride-sulfuric acid catalyst, as described in  
11 U.S. Patent No. 3,849,085. Similarly, U.S. Patent  
12 No. 4,231,759 discloses that polyalkyl hydroxyaromatic  
13 compounds may be obtained by the alkylation of phenol with  
14 polypropylene, polybutylene and other polyalkylene  
15 compounds, in the presence of an alkylation catalyst, such  
16 as boron trifluoride.  
17

18 One preferred method of preparing polyalkyl hydroxyaromatic  
19 compounds is disclosed in U.S. Patent No. 4,238,628. This  
20 patent teaches a process for producing undegraded alkylated  
21 phenols by alkylating, at about 0°C to 60°C, a complex  
22 comprising boron trifluoride and phenol with a propylene or  
23 higher olefin polymer having terminal ethylene units,  
24 wherein the molar ratio of complex to olefin polymer is  
25 about 1:1 to 3:1. Preferred olefin polymers include  
26 polybutene having terminal ethylene units.  
27

28 Preferred polyalkyl hydroxyaromatic compounds finding use in  
29 the fuel additive composition of the present invention  
30 include polypropylene phenol, polyisobutylene phenol, and  
31 polyalkyl phenols derived from polyalphaolefins,  
32 particularly 1-decene oligomers.  
33  
34

-14-

01 Polyalkyl phenols, wherein the polyalkyl group is derived  
02 from polyalphaolefins, such as 1-octene and 1-decene  
03 oligomers, are described in PCT International Patent  
04 Application Publication No. WO 90/07564, published July 12,  
05 1990, the disclosure of which is incorporated herein by  
06 reference. This publication teaches that such polyalkyl  
07 phenols may be prepared by reacting the appropriate  
08 polyalphaolefin with phenol in the presence of an alkylating  
09 catalyst at a temperature of from about 60°C to 200°C,  
10 either neat or in an inert solvent at atmospheric pressure.  
11 A preferred alkylation catalyst for this reaction is a  
12 sulfonic acid catalyst, such as Amberlyst 15®, available  
13 from Rohm and Haas, Philadelphia, Pennsylvania.  
14

15 Also contemplated for use in the present fuel additive  
16 composition are the salts of the polyalkyl hydroxyaromatic  
17 component, such as alkali metal, alkaline earth metal,  
18 ammonium, substituted ammonium and sulfonium salts.  
19 Preferred salts are the alkali metal salts of the polyalkyl  
20 hydroxyaromatic compound, particularly the sodium and  
21 potassium salts, and the substituted ammonium salts.  
22

### 23 Fuel Compositions

24

25 The fuel additive composition of the present invention will  
26 generally be employed in a hydrocarbon distillate fuel  
27 boiling in the gasoline or diesel range. The proper  
28 concentration of this additive composition necessary in  
29 order to achieve the desired detergency and dispersancy  
30 varies depending upon the type of fuel employed, the  
31 presence of other detergents, dispersants and other  
32 additives, etc. Generally, however, from 150 to 7500 weight  
33 ppm, preferably from 300 to 2500 ppm, of the present  
34

01 additive composition per part of base fuel is needed to  
02 achieve the best results.

03

04 In terms of individual components, fuel compositions  
05 containing the additive compositions of the invention will  
06 generally contain about 50 to 2500 ppm of the  
07 poly(oxyalkylene) amine and about 100 to 5000 ppm of the  
08 polyalkyl hydroxyaromatic compound. The ratio of polyalkyl  
09 hydroxyaromatic to poly(oxyalkylene) amine will generally  
10 range from about 0.5 to 10:1, and will preferably be about  
11 2:1 or greater.

12

13 The deposit control additive may be formulated as a  
14 concentrate, using an inert stable oleophilic organic  
15 solvent boiling in the range of about 150°F to 400°F.  
16 Preferably, an aliphatic or an aromatic hydrocarbon solvent  
17 is used, such as benzene, toluene, xylene or higher-boiling  
18 aromatics or aromatic thinners. Aliphatic alcohols of about  
19 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol,  
20 n-butanol and the like, in combination with hydrocarbon  
21 solvents are also suitable for use with the detergent-  
22 dispersant additive. In the concentrate, the amount of the  
23 present additive composition will be ordinarily at least 10%  
24 by weight and generally not exceed 70% by weight, preferably  
25 10 to 50 weight percent and most preferably from 10 to 25  
26 weight percent.

27

28 In gasoline fuels, other fuel additives may also be included  
29 such as antiknock agents, e.g., methylcyclopentadienyl  
30 manganese tricarbonyl, tetramethyl or tetraethyl lead, or  
31 other dispersants or detergents such as various substituted  
32 amines, etc. Also included may be lead scavengers such as  
33 aryl halides, e.g., dichlorobenzene or alkyl halides, e.g.,  
34 ethylene dibromide. Additionally, antioxidants, metal

01 deactivators, pour point depressants, corrosion inhibitors  
02 and demulsifiers may be present.

03

04 In diesel fuels, other well-known additives can be employed,  
05 such as pour point depressants, flow improvers, cetane  
06 improvers, and the like.

07

08 The following examples are presented to illustrate specific  
09 embodiments of this invention and are not to be construed in  
10 any way as limiting the scope of the invention.

11

12

### EXAMPLES

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#### Example 1

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#### Preparation of Polyisobutyl Phenol

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18 To a flask equipped with a magnetic stirrer, reflux  
19 condenser, thermometer, addition funnel and nitrogen inlet  
20 was added 203.2 grams of phenol. The phenol was warmed to  
21 40°C and the heat source was removed. Then,  
22 73.5 milliliters of boron trifluoride etherate was added  
23 dropwise. Ultravis 10 polyisobutene (molecular weight 950,  
24 76% methylvinylidene, available from British Petroleum) was  
25 dissolved in 1,863 milliliters of hexane. The polyisobutene  
26 was added to the reaction at a rate to maintain the  
27 temperature between 22-27°C. The reaction mixture was  
28 stirred for 16 hours at room temperature. Then,  
29 400 milliliters of concentrated ammonium hydroxide was added  
30 followed by 2,000 milliliters of hexane. The reaction  
31 mixture was washed with water (3 x 2,000 milliliters), dried  
32 over magnesium sulfate, filtered and the solvents removed  
33 under vacuum to yield 1,056.5 grams of a crude reaction  
34 product. The crude reaction product was determined to

-17-

01 contain 80% of the desired product by proton NMR and  
02 chromatography on silica gel eluting with hexane, followed  
03 by hexane: ethylacetate: ethanol (93:5:2).  
04

05 Example 2

06 Thermogravimetric Analysis  
07

08  
09 The stability of certain fuel additives was measured by  
10 thermogravimetric analysis (TGA). The TGA procedure  
11 employed DuPont 951 TGA instrumentation coupled with a  
12 microcomputer for data analysis. Samples of the fuel  
13 additive (approximately 25 milligrams) were heated from 25°C  
14 to 700°C at 5°C per minute under air flowing at 100 cubic  
15 centimeters per minute. The weight of the sample was  
16 monitored as a function of temperature. The thermal  
17 stability of various samples was compared at fifty percent  
18 weight loss. Sample 1 was a tetrapropenylphenyl  
19 poly(oxybutylene) ethylene diamine carbamate having a  
20 molecular weight of about 1718, prepared in a manner similar  
21 to that described in U.S. Patent No. 4,160,648 to Lewis,  
22 Examples 6-8. Sample 2 was a polyisobutyl phenol prepared  
23 from Ultravis 30 polyisobutene (molecular weight 1300, 74%  
24 methylvinylidene, available from British Petroleum) in a  
25 manner similar to Example 1 above.  
26

27 The fifty percent weight loss temperature for Sample 1,  
28 tetrapropenylphenyl poly(oxybutylene) ethylenediamine  
29 carbamate, was 259°C. The fifty percent weight loss  
30 temperature for Sample 2, polyisobutyl phenol, was 347°C. A  
31 one-to-one mixture of the two components, Samples 1 and 2,  
32 was analyzed by TGA. The twenty-five percent weight loss  
33 temperature (50% weight loss of tetrapropenylphenyl  
34 poly(oxybutylene) ethylenediamine carbamate in the mixture)

01 was 296°C. This demonstrates that the thermal stability of  
02 the tetrapropenylphenyl poly(oxybutylene) ethylenediamine  
03 carbamate is increased by the presence of the polyisobutyl  
04 phenol. This increase in thermal stability allows the  
05 tetrapropenylphenyl poly(oxybutylene) ethylenediamine  
06 carbamate to last longer at intake valve operating  
07 temperatures and allows for less deposits.

08

09

Example 1

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Engine Test

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13 A laboratory engine test was used to evaluate both intake  
14 valve and combustion chamber deposit performance of the  
15 additive composition of the invention. The test engine is a  
16 4.3 liter, TBI (throttle body injected), V6 engine  
17 manufactured by General Motors Corporation.

18

19 The major engine dimensions are listed below:

20

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Table I - Engine Dimensions	
Bore	10.16 cm
Stroke	8.84 cm
Displacement Volume	4.3 liter
Compression Ratio	9.3:1

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The test procedure involves engine operation for 40 hours  
(24 hours a day) on a prescribed load and speed schedule  
representative of typical driving conditions. The cycle for  
engine operation during the test is as follows:

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Table II - Engine Driving Cycle				
Step	Mode	Time in Mode [Sec]*	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

\* All steps except step number 3, include a 15 second transition ramp. Step 3 include a 20 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table III.

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Table III				
Laboratory Engine Test Results				
Run	Additive	Concentration, ppm	Intake Valve Deposits, mg	Combustion Chamber Deposits, mg
1	-	-	530	1,455
2	Poly (oxyalkylene) Amine <sup>a</sup>	200	471	1,692
3	Polyalkyl Phenol <sup>b</sup>	400	103	2,530
4	Poly (oxyalkylene) Amine/Polyalkyl Phenol <sup>c</sup>	200/400	18	1,825

- a: tetrapropenylphenyl poly(oxybutylene) ethylene diamine carbamate  
b: Ultravis 10 polyisobutyl (MW = 950) phenol  
c: mixture of 200 ppm tetrapropenylphenyl poly(oxybutylene) ethylene diamine carbamate and 400 ppm Ultravis 10 polyisobutyl phenol

The results shown in Table III demonstrate that the combination of polyisobutyl phenol and tetrapropenylphenyl poly(oxybutylene) ethylene diamine carbamate has a synergistic effect and gives significantly better intake valve deposit control than either component by itself. Also, the addition of tetrapropenylphenyl poly(oxybutylene) ethylene diamine carbamate to the polyisobutyl phenol reduces the combustion chamber deposit weight compared to the polyisobutyl phenol alone.

01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

04

05 (a) a poly(oxyalkylene) amine having at least one  
06 basic nitrogen atom and a sufficient number of  
07 oxyalkylene units to render the poly(oxyalkylene)  
08 amine soluble in hydrocarbons boiling in the  
09 gasoline or diesel range; and

10

11 (b) a polyalkyl hydroxyaromatic compound or salt  
12 thereof wherein the polyalkyl group has sufficient  
13 molecular weight and carbon chain length to render  
14 the polyalkyl hydroxyaromatic compound soluble in  
15 hydrocarbons boiling in the gasoline or diesel  
16 range.

17

18 2. The fuel additive composition according to Claim 1,  
19 wherein the poly(oxyalkylene) amine of component (a)  
20 has a molecular weight in the range of about 500 to  
21 about 10,000.

22

23 3. The fuel additive composition according to Claim 1,  
24 wherein the poly(oxyalkylene) amine of component (a)  
25 contains at least about 5 oxyalkylene units.

26

27 4. The fuel additive composition according to Claim 1,  
28 wherein the poly(oxyalkylene) amine of component (a) is  
29 a hydrocarbyl poly(oxyalkylene) polyamine.

30

31 5. The fuel additive composition according to Claim 1,  
32 wherein the poly(oxyalkylene) amine of component (a) is  
33 a poly(oxyalkylene) polyamine wherein the  
34 poly(oxyalkylene) moiety is connected to the polyamine

- 01 moiety through an oxyalkylene hydroxy linkage derived  
02 from an epihalohydrin.  
03
- 04 6. The fuel additive composition according to Claim 1,  
05 wherein the poly(oxyalkylene) amine of component (a) is  
06 a branched alkyl poly(oxyalkylene) monoamine wherein  
07 the branched alkyl group is derived from the product of  
08 a Guerbet condensation reaction.  
09
- 10 7. The fuel additive composition according to Claim 1,  
11 wherein the poly(oxyalkylene) amine of component (a) is  
12 a hydrocarbyl poly(oxyalkylene) aminocarbamate.  
13
- 14 8. The fuel additive composition according to Claim 7,  
15 wherein the hydrocarbyl group in component (a) contains  
16 from 1 to about 30 carbon atoms.  
17
- 18 9. The fuel additive composition according to Claim 8,  
19 wherein the hydrocarbyl group in component (a) is an  
20 alkylphenyl group.  
21
- 22 10. The fuel additive composition according to Claim 9,  
23 wherein the alkyl moiety in the alkylphenyl group is  
24 tetrapropenyl.  
25
- 26 11. The fuel additive composition according to Claim 7,  
27 wherein the amine moiety of the aminocarbamate is  
28 derived from a polyamine having from 2 to 12 amine  
29 nitrogen atoms and from 2 to 40 carbon atoms.  
30
- 31 12. The fuel additive composition according to Claim 11,  
32 wherein the polyamine is a polyalkylene polyamine  
33 having 2 to 12 amino nitrogen atoms and 2 to 24 carbon  
34 atoms.

- 01 13. The fuel additive composition according to Claim 12,  
02 wherein the polyalkylene polyamine is selected from the  
03 group consisting of ethylene diamine, propylene  
04 diamine, diethylene triamine and dipropylene triamine.  
05
- 06 14. The fuel additive composition according to Claim 7,  
07 wherein the poly(oxyalkylene) moiety of component (a)  
08 is derived from C<sub>2</sub> to C<sub>8</sub> oxyalkylene units.  
09
- 10 15. The fuel additive composition according to Claim 7,  
11 wherein the hydrocarbyl poly(oxyalkylene)  
12 aminocarbamate of component (a) is an alkylphenyl  
13 poly(oxybutylene) aminocarbamate, wherein the amine  
14 moiety is derived from ethylene diamine or diethylene  
15 triamine.  
16
- 17 16. The fuel additive composition according to Claim 1,  
18 wherein the polyalkyl hydroxyaromatic compound of  
19 component (b) has a polyalkyl group with an average  
20 molecular weight of about 400 to 5,000.  
21
- 22 17. The fuel additive composition according to Claim 1,  
23 wherein the hydroxyaromatic compound is phenol.  
24
- 25 18. The fuel additive composition according to Claim 1,  
26 wherein the polyalkyl substituent in component (b) is  
27 derived from polypropylene, polybutylene, or  
28 polyalphaolefin oligomers of 1-decene.  
29
- 30 19. The fuel additive composition according to Claim 18,  
31 wherein the polyalkyl substituent in component (b) is  
32 derived from polyisobutylene.  
33  
34

- 01 20. The fuel additive composition according to Claim 19,  
02 wherein the polyisobutylene contains at least about 20%  
03 of a methylvinylidene isomer.  
04
- 05 21. The fuel additive composition according to Claim 1,  
06 wherein component (a) is an alkylphenyl  
07 poly(oxybutylene) aminocarbamate, wherein the amine  
08 moiety is derived from ethylene diamine or diethylene  
09 triamine, and component (b) is a polyisobutyl phenol.  
10
- 11 22. A fuel composition comprising a major amount of  
12 hydrocarbons boiling in the gasoline or diesel range  
13 and an effective detergent amount of an additive  
14 composition comprising:  
15
- 16 (a) a poly(oxyalkylene) amine having at least one  
17 basic nitrogen atom and a sufficient number of  
18 oxyalkylene units to render the poly(oxyalkylene)  
19 amine soluble in hydrocarbons boiling in the  
20 gasoline or diesel range; and  
21
- 22 (b) a polyalkyl hydroxyaromatic compound or salt  
23 thereof wherein the polyalkyl group has sufficient  
24 molecular weight and carbon chain length to render  
25 the polyalkyl hydroxyaromatic compound soluble in  
26 hydrocarbons boiling in the gasoline or diesel  
27 range.  
28
- 29 23. A fuel concentrate comprising an inert stable  
30 oleophilic organic solvent boiling in the range of from  
31 about 150°F to 400°F and from about 10 to 70 weight  
32 percent of an additive composition comprising:  
33  
34

- 01 (a) a poly(oxyalkylene) amine having at least one  
02 basic nitrogen atom and a sufficient number of  
03 oxyalkylene units to render the poly(oxyalkylene)  
04 amine soluble in hydrocarbons boiling in the  
05 gasoline or diesel range; and  
06  
07 (b) a polyalkyl hydroxyaromatic compound or salt  
08 thereof wherein the polyalkyl group has sufficient  
09 molecular weight and carbon chain length to render  
10 the polyalkyl hydroxyaromatic compound soluble in  
11 hydrocarbons boiling in the gasoline or diesel  
12 range.  
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# INTERNATIONAL SEARCH REPORT

PCT/US93/02038

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C10L 1/22  
US CL : 044/387,442,450

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 044/387,442,450

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 3,849,085 (Kreuz et al.) 19 November 1974 See Col. 2, lines 3-61.	1-23
A	US,A, 4,134,846 (Machleder et al.) 16 January 1979 See col. 1, lines 36-59 and col. 2 lines 30-64.	1-23
A	US,A, 4,191,537 (Lewis et al.) 04 March 1980 See claims.	1-23
A	US,A, 4,270,930 (Campbell et al.) 02 June 1981 See the entire document.	1-23
A	US,A, 4,778,481 (Courtney) 18 October 1988 See claims.	1-23

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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* E		earlier document published on or after the international filing date
* L	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)
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* P	* Z	document member of the same patent family
		document published prior to the international filing date but later than the priority date claimed

Date of the actual completion of the international search  
10 MAY 1993

Date of mailing of the international search report  
17 JUL 1993

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/02038

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,881,945 (Buckley, III) 21 November 1989 See the entire document.	1-23
A	US,A, 4,933,485 (Buckley, III) 12 June 1990 See the entire document.	1-23